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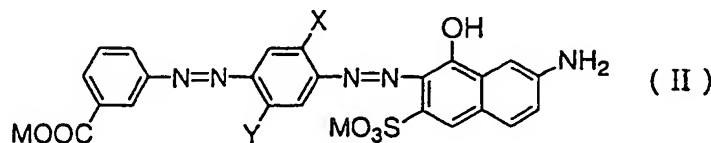
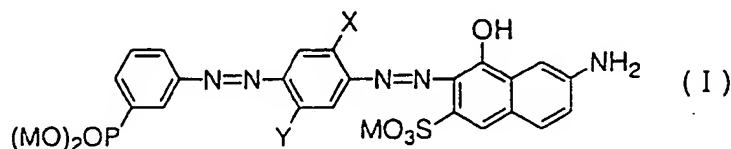
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(54) Disazo-dye composition and black aqueous ink composition containing the same

(57) A disazo dye composition comprising at least a disazo dye represented by formula (I) and a disazo dye represented by formula (II);



(wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of, alkaline metal, NH₄, alkyl-substituted ammonium, alkanolammonium, morpholinium and piperidinium), wherein, when the disazo dye composition is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by formula (I) to the peak area (Sc) of the disazo dye represented by formula (II), that is Sp : Sc is from 1 : 0.4 to 1 : 2.4. This disazo dye composition provides a high quality image, rapid ink fixing and the like even on the plain paper.

Description

The present invention relates to a disazo dye composition, a black aqueous ink composition containing the same and a inkjet recording method using the same.

5 The ink used in an inkjet recording method is usually obtained by dissolving a variety of dyes in water or an organic solvent or a mixture thereof, but various more strict performances are required as compared with the ink for writing instruments such as a fountain pen and a ball-point pen, in various characteristics.

Further, as a recent trend, output by an inkjet printer is eagerly required to offer a high quality image (a sharp image having high optical density and no bleeding), high speed printing, and water resistance and light resistance of the print.

10 Then, to realize high speed printing, rapid fixing of the ink is required. Therefore, attempts were made to improve penetrability of ink into a recording medium. Japanese kokai publication 183761/1992, USP No. 5,156,675, USP No. 5,183,502 and the like, for example, disclose the addition of diethylene glycol monobutyl ether, addition of both glycol ethers and a nonionic acetylene glycol surface active agent, and the like.

The permeable ink disclosed herein, however, when it is used for recording on plain paper, the surface of which is not particularly treated (copy paper, report paper, bond paper, letter paper, postcards, sales slips and the like used in the office, school, home), gives poor colour development, since the ink permeates into the paper. Therefore, it was difficult to obtain a sharp image having high optical density. When the dye concentration is increased in order to solve this problem, reliability of the ink becomes poor and clogging may occur. Therefore, dyes used in permeable inks are required to have extremely high solubility.

20 On the other hand, regarding the requirement of water resistance of the print, a lot of inks are said to have excellent water resistance, such as the aqueous ink containing a dye having a phosphoric group disclosed in Japanese kokoku publication 30956/1993, the ink containing a disazo dye having a carboxyl group and the like disclosed in Japanese kokai publication 91577/1991, Japanese kokai publication 262998/1993 and the like.

25 However, though the ink disclosed is excellent in water resistance, when used for recording on an acidic paper, pH of which surface is in an acidic range, a brownish image is obtained and the density of the image becomes low, therefore, a high grade image can not be obtained. Further, there is a problem that clogging is prone to occur in fine discharge orifices of an inkjet head due to insufficient solubility of the dye in a liquid medium, therefore, the dyes are not appropriate for the permeable ink.

In addition, a variety of ink compositions having excellent water resistance by using known dyes, have been made. However, an ink has not been provided which suffices both enough water resistance and high grade image.

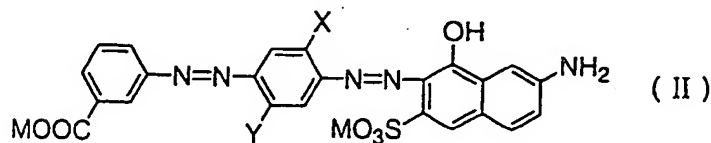
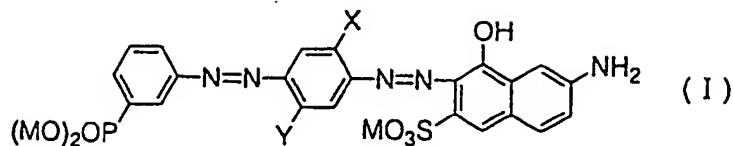
30 An object of the invention is to provide a dye composition and an ink composition which give a high grade image (a sharp image having high optical density and no bleeding), rapid fixing of the ink, water resistance and light resistance, even when it is printed on the plain paper.

35 As a solution of this problem, it has been found that the above-described high grade image and water resistance are simultaneously satisfied by using, as a recording agent of the ink, a composition obtained by selecting two aqueous dyes having similar structures and excellent characteristics from among known black disazo dyes and mixing these dyes at a certain ratio, or a composition synthesized directly as a dye composition.

The present invention will become more fully understood from the detailed description given hereinbelow and accompanying drawings which are given by way of illustration only, and wherein:

- 40 Figure 1 is the chromatogram of the dye composition 1 obtained in Example 1;
 Figure 2 is the visual light spectrum of the dye composition 1 obtained in Example 1;
 Figure 3 is the chromatogram of the dye composition 2 obtained in Example 2;
 Figure 4 is the chromatogram of the dye composition 3 obtained in Example 3;
 45 Figure 5 is the chromatogram of the dye composition 4 obtained in Example 4;
 Figure 6 is the chromatogram of the dye composition 5 obtained in Example 5;
 Figure 7 is the chromatogram of the dye composition obtained in Comparative Example 1;
 Figure 8 is the visual light spectrum of the dye composition obtained in Comparative Example 1;
 Figure 9 is the chromatogram of the dye composition obtained in Comparative Example 2;
 50 Figure 10 is the visual light spectrum of the dye composition obtained in Comparative Example 2.
 Figure 11 is the chromatogram of the mixed dye concentrated liquid F obtained in Example 11.
 Figure 12 is the graph which illustrates the gradient condition of the liquid chromatography.

55 The present invention relates to a disazo dye composition comprising at least a disazo dye represented by the formula (I) and a disazo dye represented by the formula (II):



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(wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of, alkaline metal, NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium, piperidinium and the like), wherein, when the disazo dye composition is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by the formula (I) to the peak area (Sc) of the disazo dye represented by the formula (II), that is $\text{Sp} : \text{Sc}$ is from 1 : 0.4 to 1 : 2.4, preferably from 1 : 0.6 to 1 : 1.5, and an ink composition using the same.

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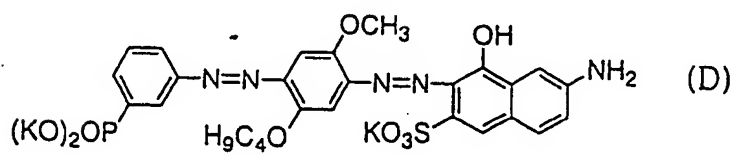
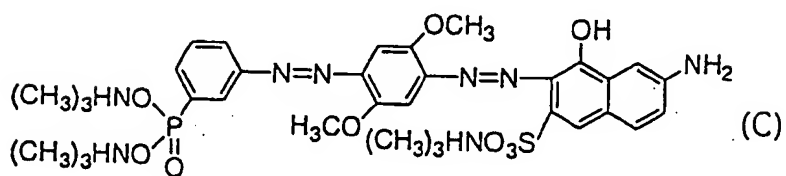
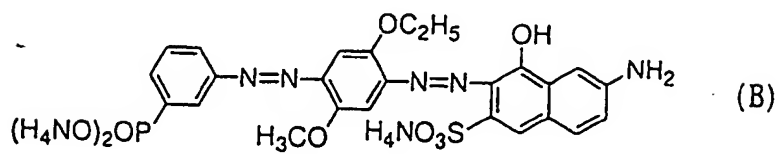
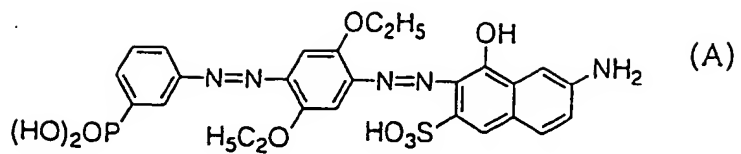
As an alkoxy group represented by X and Y in the dyes represented by the above-mentioned formulae (I) and (II) used in the present invention, for example, a methoxy group, ethoxy group, propoxy group and butoxy group are listed. Alkoxy groups X and Y may be the same or different.

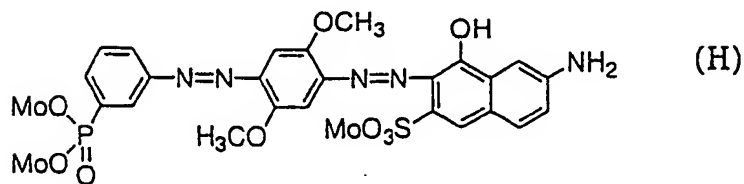
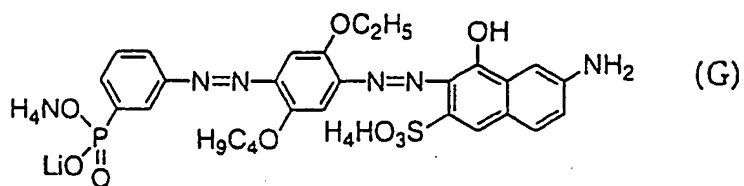
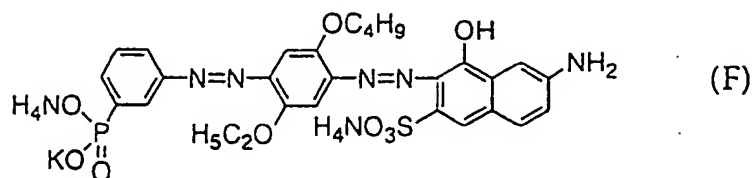
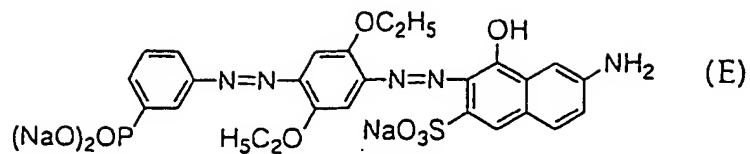
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M is selected from hydrogen, alkaline metal, NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium, piperidinium and the like.

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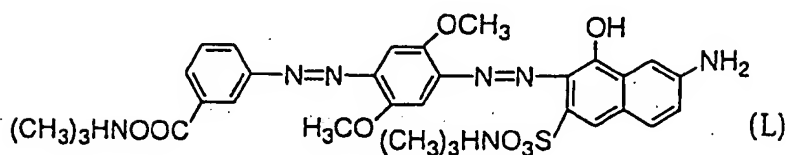
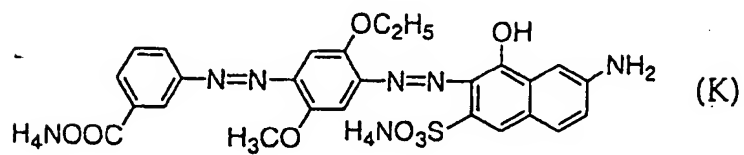
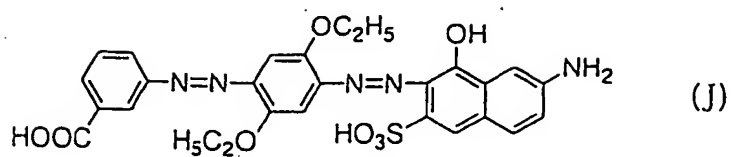
Specific examples of the disazo dye compounds employed in the present invention are listed below. The followings are examples of dye compounds of formula (I).

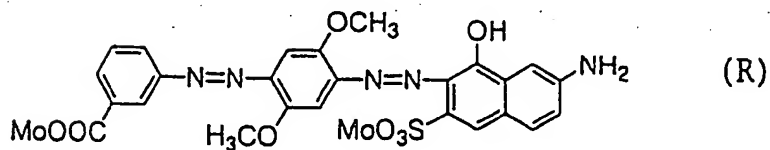
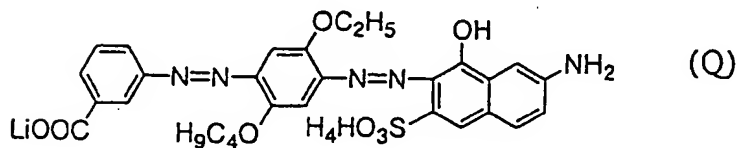
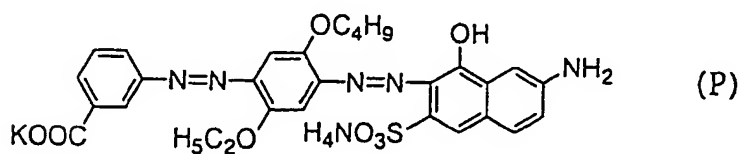
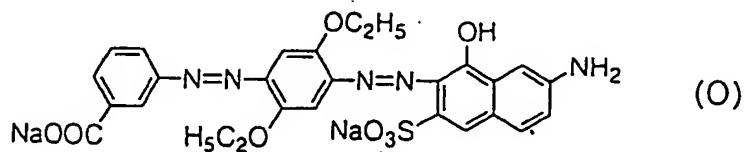
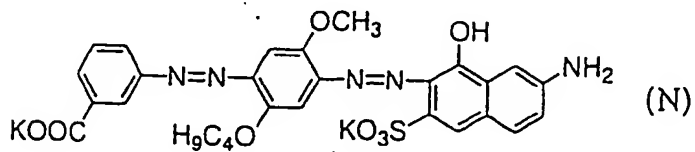




Mo , represents morpholinium

The followings are examples of dye compounds of formula (II).





Mo represents morpholinium

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In the formula (I) and (II), when M represents hydrogen, the water soluble acid group is in the form of the free acid. Specifically, each of which represents a phosphoric acid group (PO₃H₂), carboxyl group (COOH), sulfonic acid group (SO₃H). When M represents a cation such as an alkaline metal, NH₄, alkyl-substituted ammonium, alkanolammonium, or a nitrogen-containing cyclic compound (e.g., morpholinium and piperidinium), the acid group forms a alkaline metal

salt, ammonium salt, alkyl-substituted ammonium salt, alkanolamine salt, morpholinium salt, piperidinium salt and the like, and the dye compounds become soluble to water. In general, this kind of acidic dye is soluble in an aqueous medium mainly comprising water, which shows pH in a basic range. In this case, M may be the same or different.

Furthermore, it has been found that extremely excellent water resistance on paper is obtained when M forms an alkaline salt with volatile bases such as NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium, piperidinium and the like. Examples of amines used for forming such salts include alkyl-substituted amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, isopropylamine, dipropylamine, diisopropylamine, butylamine, isobutylamine, sec-butylamine, tert-butylamine, dibutylamine; alkanolamines such as ethanolamine, diethanolamine, triethanolamine, propanolamine, diethylethanolamine; nitrogen-containing cyclic compounds such as morpholine, piperidine; and a mixture thereof. However, the whole dye of the present invention does not have to be ammonium salt, alkyl-substituted ammonium salt, alkanolammonium salt, morpholinium salt or piperidinium salt completely, and may be a mixture with alkaline metal salts. In such case, the proportion of the alkaline metal salts in whole dye is preferably not more than 50% by weight.

The disazo dye represented by the above-mentioned formula (I) having a phosphoric group is for example included in the dye group disclosed in Japanese kokoku publication 80956/1993. For synthesis of this dye, m-aminobenzenephosphonic acid is diazotized in a usual method, and it is coupled with 2,5-dialkoxy-substituted aniline having 1 to 4 carbon atoms to form a monoazo compound having an amino group. Thus obtained monoazo compound is isolated, or subsequently is diazotized in a usual way, and coupled with γ acid (2-amino-8-naphthol-6-sulfonic acid) to easily obtain the dye in high yield and high purity.

Also, the disazo dye represented by the above-mentioned formula (I) has excellent dyeing ability on cellulose fibers such as paper and shows excellent water resistance, because the dye has a phosphoric group in the dye structure. Further, since the dye also has a water soluble acid group such as a sulfonic acid group at the same time, the solubility in an aqueous liquid medium is excellent. The solubility in water of the dye differs depending on pH of the aqueous solvent, and it shows excellent solubility at pH of from 7.5 to 11, preferably from 8.5 to 10 and the solubility becomes poor at pH in an acidic range.

However, if an ink for inkjet recording is prepared by using such a disazo dye alone, the optical density of the image is insufficient. There is also a problem regarding the solution stability of the dye that clogging may occur when the dye concentration is increased in order to improve the optical density.

The disazo dye represented by the above-mentioned formula (II) having a carboxyl group is for example disclosed in Japanese kokai publication 262998/1993 or Japanese kokai publication 125318/1993. For synthesis of this dye, m-aminobenzenecarboxylic acid is diazotized in a usual method, and it is coupled with 2,5-dialkoxy-substituted aniline having 1 to 4 carbon atoms to form a monoazo compound having an amino group. Thus obtained monoazo compound is isolated, or subsequently is diazotized in a usual way, and coupled with γ acid (2-amino-8-naphthol-6-sulfonic acid) to easily obtain the dye in high yield and high purity.

Also, the disazo dye represented by the above-mentioned formula (II) has excellent water resistance, because the dye has a carboxyl group in the dye structure. Further, since the dye also has a water soluble acid group such as a sulfonic acid group at the same time, the dye is dissolved in an aqueous liquid medium in the form of an alkaline metal salt or ammonium salt. Since the dye is insoluble at pH of not more than 6, a pH of from 8.0 to 10 is preferable.

However, if the ink for inkjet recording is prepared using such a disazo dye alone, the optical density of the image is insufficient. There is also a problem regarding the solution stability of the dye that clogging may occur when the dye concentration is increased in order to improve the optical density.

It has been found that, however, by mixing the disazo dye represented by formula (I) and the disazo dye represented by formula (II) at a certain ratio, the solubility of the mixture of these dyes remarkably increases. Owing to this discovery, both high grade image (a sharp image having a high optical density and no bleeding) and high reliability have been realized, even if it is printed on the plain paper. Further, because of the water resistance and light resistance of the dyes themselves, the objects of the present invention have been solved.

The dye composition of the present invention essentially comprises the disazo dye represented by formula (I) and the disazo dye represented by formula (II), and when the dye composition is analyzed by liquid chromatography, the area ratio of the peak area (S_p) of the disazo dye represented by formula (I) to the peak area (S_c) of the disazo dye represented by formula (II), that is $S_p : S_c$ is from 1 : 0.4 to 1 : 2.4, preferably from 1 : 0.6 to 1 : 1.5.

Especially when the ink for inkjet recording is produced, the workability of the ink production is considered, and a dense liquid having an ink concentration of not less than 10% by weight is often used. When the area ratio of S_c to S_p is not more than 0.4, the dye represented by formula (I) causes a problem regarding the solution storage stability. And when the area ratio of S_c to S_p is not less than 2.4, the dye represented by formula (II) causes a problem regarding the solution storage stability.

It has been found that the area ratio $S_p : S_c$ at which the dye composition of the present invention shows excellent solution storage stability in a basic aqueous liquid medium is in the range of from 1 : 0.6 to 1 : 1.5.

The peak area ratio $S_p : S_c$ in the present invention is the ratio of the area S_p of the peak portion indicating the disazo dye represented by formula (I) to the area S_c of the peak portion indicating the disazo dye represented by for-

mula (II) observed in (high performance) liquid chromatography analysis. The conditions for the analysis are as follows.

Column

- 5 Packing: ODS (L-column)
Size: 4.6 × 250 mm

Elution Solution

- 10 A: 10% CH₃CN aqueous solution containing 0.02 N KH₂PO₄
B: 70% CH₃CN aqueous solution

Measurement

- 15 Flow rate: 1.2 ml/min
Pressure: ca 120 Kgf/cm²
Temperature: 45°C
Detecting wavelength: 313 nm

- 20 Gradient (See Fig. 12)

Initial concentration of solution B: 10%

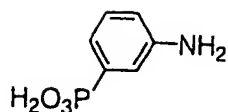
Final concentration of solution B: 70%

Gradient time: 20 min

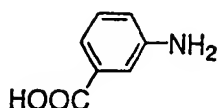
- 25 (After that, elution is conducted at the same concentration for 5 min.)

Further, when the dye composition of the present invention is analyzed by the liquid chromatography using a detecting wavelength of 313 nm, the sum (Sp + Sc) of the peak areas of the disazo dye represented by the above-mentioned formula (I) and the disazo dye represented by the above-mentioned formula (II) is not less than 90%, preferably is not less than 95% of the sum of all the peak areas. If the sum (Sp + Sc) of the peak areas is not more than 90%, the object of the present invention may not be attained.

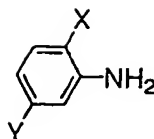
To produce the dye composition of the present invention which suffice the above-mentioned dye solution characteristic (solution storage stability), the above-mentioned disazo dye represented by formula (I) and the above-mentioned disazo dye represented by formula (II) may be individually synthesized and mixed. However, in order to simplify the synthetic process of the dyes, the simultaneous diazotization reaction of the mixed amine comprising m-aminobenzenephosphonic acid ① and m-aminobenzenecarboxylic acid ②, and successively, the coupling reaction with 2,5-dialkoxy-substituted aniline ③ used as the first coupler can, preferably be conducted, in usual methods. Regarding reaction conditions, it is preferable to diazotize at a temperature of from 0 to 5°C and to couple at a temperature of from 0 to 5°C and pH of from 0.5 to 3.5. The diazotization of the above-mentioned monoazo compound ④ and the coupling reaction with γ acid ⑤ (2-amino-8-naphthol-6-sulfonic acid) used as the second coupler are not particularly limited, and can be conducted in usual ways. Regarding the reaction conditions, it is preferable to diazotize at a temperature of from 25 to 35°C and to couple at a temperature of from 5 to 15°C and pH of from 9 to 10.



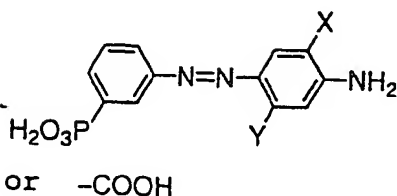
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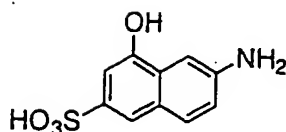
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③



④



⑤

The dye concentrated liquid of the present invention comprises the above-mentioned disazo dye composition or the dye mixture comprising the above-mentioned disazo dye represented by formula (I) and the above-mentioned disazo dye represented by formula (II) in a mixing ratio of from 1 : 0.4 to 1 : 2.4, preferably from 1 : 0.6 to 1 : 1.5 and an aqueous medium mainly comprising water, and has a dye concentration of not less than 10% by weight.

The ink composition of the present invention comprises at least the disazo dye represented by formula (I) and the disazo dye represented by formula (II), and their mixing ratio is from 1 : 0.4 to 1 : 2.4, preferably from 1 : 0.6 to 1 : 1.5 in terms of the area ratio $Sp:Sc$ (Sp indicates a peak area of formula (I) and Sc indicates a peak area of formula (II)) in liquid chromatography analysis. Therefore, the solution stability of the ink composition is extremely improved, and, both high optical density of the image and high reliability with respect to clogging and the like can be achieved.

The dyes represented by formulae (I) and (II) of the present invention, either alone or in the form of a dye composition mixed at a ratio defined in the present invention, provide excellent water resistance and colour development and improved solution storage stability and the like, by combining with a nitrogen-containing cyclic compound.

As examples of the nitrogen-containing cyclic compound, 1,3-dimethyl-2-imidazolidinone, 2-pyrrolidone, N-methyl-2-pyrrolidone, ϵ -caprolactam and the like are listed, and they are used alone or in combination of more than one. These cyclic compounds have functions as a colour development aid and a water resistance aid, as well as they improve solution stability and printing stability of the dye. They are particularly preferred cyclic compounds for the ink composition of the present invention. The amount of addition is from 1 to 30% by weight, preferably from 3 to 20% by weight.

If the amount of the addition is less than 1% by weight, above-mentioned functions can not be manifested, and more than 30% by weight, bleeding and deterioration in quality of the image may occur, these phenomena being preferable.

However, these nitrogen-containing cyclic compounds are poor in moisture retention ability, namely wettability. Therefore, when these nitrogen-containing cyclic compounds are used alone as an aid of the solution stability, clogging is apt to occur, and once clogging occurs, it is difficult to recover. Then, it is preferred that an anti-clogging agent (humectant) is used in combination. As the anti-clogging agent (humectant), polyhydric alcohols are preferred. Meanwhile, if the polyhydric alcohols are used alone as the aid of the solution stability, the water resistance of the ink becomes poor and the colour development characteristic becomes inferior. Therefore, it is particularly preferred that the dye represented by the general formulae (I) and (II), polyhydric alcohols and a nitrogen-containing cyclic compound are combined in the ink composition of the present invention.

As examples of the polyhydric alcohols, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, 1,3-propanediol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerin and the like are listed, and they are used alone or in combination of more than one. The amount of addition is from 1 to 30% by weight, preferably from 3 to 20% by weight.

If the amount of addition is less than 1% by weight, clogging occurs which is difficult to recover, and more than 30% by weight, drying time of the image lowers and the quality of the image deteriorates, these phenomena being preferable.

There is large difference in the solution storage stability of the ink, between the case in which the dyes of formulae (I) and (II) are respectively used alone and the case in which they are mixed, and it is not preferred to use the dyes of

formulae (I) and (II) respectively alone in order to secure the reliability of the ink.

It is preferred that the ink composition of the present invention contains a nonionic acetylene glycol surface active agent. The additive is effective in keeping roundness of one dot of the discharged ink, as well as it gives fast penetration of the ink.

Specific nonionic acetylene glycol surface active agents used in the present invention include, for example, SURFINOL 465, SURFINOL 104, OLFIN STG (they are all trade names of the products available from Nisshin Chemical Corp.) and the like, and the particularly preferred is OLFIN STG. The amount of addition is from 0.05 to 3% by weight, preferably from 0.5 to 2% by weight. If the amount of addition is less than 0.05% by weight, sufficient penetrability can not be obtained, and more than 30% by weight, bleeding occurs in an image and quality of the image deteriorates, these phenomena being undesirable.

Further, by addition of glycol ethers in addition to the nonionic acetylene glycol surface active agent, the penetration further increases, and therefore, bleeding through the boundary of adjacent color ink when colour printing is conducted, decreases, and a very sharp image can be obtained.

Examples of glycol ethers of the present invention include ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, dipropylene glycol monoethyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, triethylene glycol monobutyl ether and the like. The amount of addition is from 3 to 30% by weight, preferably from 5 to 15% by weight. If the amount of addition is less than 3% by weight, effect of anti-bleeding can not be obtained. And more than 30% by weight, bleeding of an image may occur. Furthermore, oily separation of the ink may occur, and a solution aid such as the glycol ether is required, consequently viscosity of the ink increase, and discharge by the inkjet head becomes difficult.

The ink composition of the present invention may be, if necessary, added with lower alcohols, pH regulators such as triethanolamine, alkaline metal hydroxide and the like, water soluble polymers such as sodium alginate and the like, water soluble resin, fluorine containing surface active agent, antifungal agent, anticorrosion agent and the like.

The ink production using the above-mentioned ink composition can be conducted according to a usual method. For example, there is a method in which each ingredient is fully mixed and dissolved, after pressure filtration through a membrane filter having a pore diameter of 0.8 μm , deaeration treatment is applied using a vacuum pump to prepare the ink composition.

Next, the recording method of the present invention using the above-mentioned ink is explained. The preferred recording method is the inkjet recording method in which the ink is discharged through fine orifices as droplets. But, the ink composition of the present invention can be applied for general writing instruments, recorder, penplotter and the like.

As the inkjet recording method, any known methods can be used, especially, excellent image recording is provided in a method in which liquid droplets are discharged by using vibration of a piezoelectric element or by using heat energy.

The dye composition of the present invention comprises two disazo dye components having similar structures in the well-balanced mixing ratio.

Therefore, a dye composition and an ink composition which give high grade image (a sharp image having high optical density and no bleeding), rapid fixing of the ink, water resistance and light resistance, is provided.

Further, with the dye composition of the present invention, high quality recording is possible and water resistance of a recorded image can be obtained, especially on the plain paper such as copy paper, report paper, bond paper, letter paper, postcards, sales slips and the like used in the office, school or home.

Examples

The present invention will be further explained in detail in the following examples and comparative examples.

First, the method for producing the ink composition of the present invention is explained in the following examples 1 to 5 and comparative examples 1 and 2.

Example 1

A mixed amine of 17.5 g (0.1 mol) of m-aminobenzenephosphonic acid and 13.85 g (0.1 mol) of m-aminobenzene-carboxylic acid was suspended in 400 ml of water under stirring, to this was added 30.4 g (0.29 mol) of 35% hydrochloric acid, and the resulting solution was cooled to 0°C. To this solution was added 40.0 g (0.21 mol) of 36% sodium nitrite aqueous solution gradually so that the temperature does not exceed 5°C, and the obtained solution was stirred for 50 minutes to diazotize the mixed amine, subsequently thiourea was added to the resulted aqueous solution, and excessive nitrous acid was removed to obtain a diazo-component containing liquid. Separately, 36.3 g (0.22 mol) of 2,5-diethoxyaniline was dispersed in 500 ml of water, and 21.3 g (0.21 mol) of 35% hydrochloric acid was added to dissolve the aniline to obtain a coupling-component containing liquid. Here, the coupling-component containing liquid was cooled to 0°C, to this was added above-mentioned diazo-component containing liquid dropwise so that the temperature does not exceed 5°C. Subsequently, the resulting mixture was stirred for 20 hours at 3 to 5°C to obtain a monoazo compound (mixture).

m-(2,5-diethoxy-4-amino-phenylazo)benzenephosphonic acid and m-(2,5-diethoxy-4-phenylazo)benzenecarboxylic acid.

The resulted monoazo compound mixture was dispersed in 900 ml of water, and 43.0 g (0.48 mol) of 45% sodium hydroxide aqueous solution was added to make a solution. To this solution was added 38.5 g (0.20 mol) of 36% sodium nitrite aqueous solution and cooled to 25°C, after further gradual addition of 130 g (0.71 mol) of 20% hydrochloric acid so that the temperature does not exceed 30°C, the resulting mixture was stirred for 3 hours at 25 to 30°C to diazotize the monoazo compound mixture. Then, to the resulted aqueous solution was added sulfamic acid, and excessive nitrous acid was removed to obtain a diazo-component liquid.

Separately, 51.6 g (0.21 mol) of γ acid was added to 600 ml of water, and 37.0 g (0.42 mol) of 45% sodium hydroxide aqueous solution was added to make a solution, and the solution was cooled to prepare a coupler solution. To this, the previously prepared diazo-component containing liquid of the monoazo compound was added dropwise so that the reaction temperature does not exceed 8°C and reaction pH is kept not less than 8.5 by the addition of 20% sodium hydroxide aqueous solution, then the mixture was stirred for 3 hours at 8°C. By salt/acid deposition treatment, about 75 g of a dye composition 1 mainly comprising the above-mentioned two disazo dyes represented by (A) and (J) was obtained.

When the resulted dye composition 1 was analyzed by high performance liquid chromatography (HPLC). The area ratio $S_p : S_c$ of the disazo dye (A) to the disazo dye (J) was 50.4 : 49.6 (1 : 0.98). This chromatogram is shown in Figure 1. And the sum of the peak areas ($S_p + S_c$) of the resulted disazo dyes was about 99% of the total area when a detecting wavelength is 313 nm.

The liquid chromatography analysis was conducted according to the above described conditions, by using the following apparatuses.

Contoroller: SCL-6A
 Detector: SPD-6AV
 Pump unit: LC-6A (x2)
 Column oven: CTO-6A
 Plotter: C-R6A

The peak area ratio S_p/S_c of the disazo dyes represented by the formulae (I) and (II) was calculated based on the peak area analyzed by the plotter. The following are the parameters for analysis of the plotter.

WIDTH: 5 SLOPE: 330
 DRIFT: 0 MIN. AREA: 4000
 T. DBL: 5 STOP TIME: 25
 ATTEN: 6 SPEED: 2

The sample was prepared by dissolving 3 mg of the dye composition (ammonium salt) into 50 ml of a carrier liquid. And visual light absorption spectrum of the dye composition 1 was shown in Figure 2.

Example 2

The same procedure as Example 1 was carried out, except that a mixed amine of 21.00 g (0.12 mol) of m-aminobenzenephosphonic acid and 11.08 g (0.08 mol) of m-aminobenzenecarboxylic acid was used instead of the mixed amine used in Example 1, to obtain about 76 g of dye composition 2 mainly comprising the above-mentioned two disazo dyes represented by the formulae (A) and (J).

When the resulted dye composition 2 was analyzed by high performance liquid chromatography, the area ratio $S_p : S_c$ of the disazo dye (A) to the disazo dye (J) was 56.0 : 44.0 (1 : 0.79). This chromatogram is shown in Figure 3. And the sum of the peak areas ($S_p + S_c$) of the resulted disazo dyes was about 99% of the total area when a detecting wavelength is 313 nm.

Example 3

The same procedure as Example 1 was carried out, except that a mixed amine of 14.00 g (0.08 mol) of m-aminobenzenephosphonic acid and 16.62 g (0.12 mol) of m-aminobenzenecarboxylic acid was used instead of the mixed amine used in Example 1, to obtain about 73 g of dye composition 3 mainly comprising the above-mentioned two disazo dyes represented by the formulae (A) and (J).

When the resulted dye composition 3 was analyzed by high performance liquid chromatography, the area ratio $S_p : S_c$ of the disazo dye (A) to the disazo dye (J) was 33.8 : 66.2 (1 : 1.96). This chromatogram is shown in Figure 4. And the sum of the peak areas ($S_p + S_c$) of the resulted disazo dyes was about 99% of the total area when a detecting wave-

length is 313 nm.

Example 4

5 The same procedure as Example 1 was carried out, except that a mixed amine of 24.50 g (0.14 mol) of m-aminobenzene phosphonic acid and 8.31 g (0.06 mol) of m-aminobenzenecarboxylic acid was used instead of the mixed amine used in Example 1, to obtain about 77 g of dye composition 4 mainly comprising the above-mentioned two disazo dyes represented by the formulae (A) and (J).

10 When the resulted dye composition 4 was analyzed by high performance liquid chromatography, the area ratio S_p : S_c of the disazo dye (A) to the disazo dye (J) was 64.4 : 35.6 (1 : 0.55). This chromatogram is shown in Figure 5. And the sum of the peak areas ($S_p + S_c$) of the resulted disazo dyes was about 99% of the total area when a detecting wavelength is 313 nm.

Example 5

15 The same procedure as Example 1 was carried out, except that a mixed amine of 10.50 g (0.06 mol) of m-aminobenzene phosphonic acid and 19.39 g (0.14 mol) of m-aminobenzenecarboxylic acid was used instead of the mixed amine used in Example 1, to obtain about 72 g of dye composition 5 mainly comprising the above-mentioned two disazo dyes represented by the formulae (A) and (J).

20 When the resulted dye composition 5 was analyzed by high performance liquid chromatography, the area ratio S_p : S_c of the disazo dye (A) to the disazo dye (J) was 24.0 : 76.0 (1 : 3.17). This chromatogram is shown in Figure 6. And the sum of the peak areas ($S_p + S_c$) of the resulted disazo dyes was about 99% of the total area when a detecting wavelength is 313 nm.

The above-mentioned examples are summarized and shown in Table 1.

[Table 1]

Synthesis of dye composition and analysis thereof by using high performance liquid chromatography

	Diazo component mixed amine	First coupler	Second coupler	Peak area ratio
Examples 1 to 5	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>①</p> </div> <div style="text-align: center;"> <p>②</p> </div> </div> <p>(Reaction molar ratio)</p>			HPLC detecting wavelength 313 nm Sp/Sc
1	0 : 0 = 0.5 : 0.5 (1.0)	1	1	50.4/49.6
2	0 : 0 = 0.6 : 0.4 (1.5)	1	1	56.0/44.0
3	0 : 0 = 0.4 : 0.6 (0.67)	1	1	33.8/66.2
4	0 : 0 = 0.7 : 0.3 (2.33)	1	1	64.4/35.6
5	0 : 0 = 0.3 : 0.7 (0.43)	1	1	24.0/76.0

Next, synthesis of a disazo dye composition comprising either the above-mentioned disazo dye represented by the formula (I) or the above-mentioned disazo dye represented by the formula (II) included in the dye composition of the present invention, is explained below as comparative examples.

Comparative Example 1

The same procedure as Example 1 was carried out, except that 34.62 g (0.20 mol) of m-aminobenzenephosphonic acid was used instead of the mixed amine used in Example 1, to obtain about 80 g of the disazo dye represented by the above-mentioned formula (A).

The resulted dye composition was analyzed by high performance liquid chromatography. This chromatogram is shown in Figure 7.

The visual light absorption spectrum of the disazo dye is shown in Figure 8.

Comparative Example 2

The same procedure as Example 1 was carried out, except that 27.40 g (0.20 mol) of m-aminobenzenecarboxylic acid was used instead of the mixed amine used in Example 1, to obtain about 70 g of disazo dye represented by the above-mentioned formula (J).

The resulted dye composition was analyzed by high performance liquid chromatography. This chromatogram is shown in Figure 9.

The visual light absorption spectrum of the disazo dye is shown in Figure 10.

Then, concentrated liquids having a dye concentration of not less than 10% by weight, comprising the dye composition of the present invention, are explained in the following Examples 6 to 10.

Example 6

A wet cake (dye content is about 25% by weight) before dry, obtained by the procedure of Example 1 was redispersed in ion exchanged water, this dispersion was purified and concentrated by using a reverse osmosis membrane (NTR-7410 made by Nitto Denko Corp.), and made into a dye concentrated liquid A comprising 15% by weight of the dye in the form of ammonium salt or sodium salt by using aqueous ammonia or aqueous sodium hydroxide.

The resulting dye concentrated liquid A was subjected to the following solution storage stability test of two months. The result is shown in Table 2.

(Method for solution storage stability test of dye concentrated liquid)

100 ml of the resulted dye concentrated liquid was charged into a heat resistant glass bottle, the glass bottle was sealed and allowed to stand for two months in an incubator set at 60°C. After that, the dye concentrated liquid was dropped on a filter paper to make a spot, and deposition of the dye was observed, and the result was evaluated as follows.

- ⊙: no deposition of the dye is recognized at all.
- : slight deposition of the dye is recognized.
- x: deposition of the dye is recognized.

Examples 7 to 10

The wet cakes before drying obtained according to the method of the above-mentioned Examples 2 to 5 were subjected to the same procedure as in Example 6 to obtain dye concentrated liquids each having a dye concentration and a counter ion shown in Table 2.

The resulted dye concentrated liquids B to E were subjected to the solution storage stability test of two months. The results are shown in Table 2.

Comparative Examples 3 to 4

The wet cakes before drying obtained according to the method of the above-mentioned Comparative Examples 1 to 2 were subjected to the same procedure as in Example 6 to obtain dye concentrated liquids each having a dye concentration and a counter ion shown in Table 2.

The resulted dye concentrated liquids "a" and "b" were subjected to the solution storage stability test of two months. The results are shown in Table 2.

Further, by using the above-mentioned dye example (A) obtained in the Comparative Example 1 and the above-mentioned dye example (J) obtained in the Comparative Example 2, the following mixed dye concentrated liquids each comprising 15% by weight of the dye in the form of ammonium salt were respectively prepared using ammonia water.

Example 11

Mixed dye concentrated liquid F; (A) : (J) = 5 : 5

Mixed dye concentrated liquid G; (A) : (J) = 6 : 4

Mixed dye concentrated liquid H; (A) : (J) = 4 : 6

Mixed dye concentrated liquid I; (A) : (J) = 7 : 3

Mixed dye concentrated liquid J; (A) : (J) = 3 : 7

The resulted dye concentrated liquids F to J and respective mixed dye concentrated liquid shown in Table 2 were subjected to the solution storage stability test of two months. The results are shown in Table 2.

[Table 2]

Solution storage stability test of dye concentrated liquid						
Example -	Ammonium salt				Na salt	Dye of concentrated liquid
	12%	14%	15%	16%	13%	
Example 6	⊙	⊙	⊙A	o	⊙	Dye composition 1
Example 7	⊙	⊙	⊙B	o	⊙	Dye composition 2
Example 8	⊙	⊙	oC	x	⊙	Dye composition 3
Example 9	⊙D	o	o	x	⊙	Dye composition 4
Example 10	xE	-	-	-	o	Dye composition 5
Comparative Example 3	x	-	xa	-	x	Disazo dye of Comparative Example 1
Comparative Example 4	x	-	xb	-	x	Disazo dye of Comparative Example 2
Example 11	⊙	⊙	⊙F	-	⊙	Mixed dye f
	⊙	⊙	oG	-	⊙	Mixed dye g
	⊙	⊙	oH	-	⊙	Mixed dye h
	⊙	o	oI	-	o	Mixed dye i
	⊙	o	oJ	-	o	Mixed dye j
Examples 6 to 10; dye composition concentrated liquid Comparative Example 3; concentrated liquid of disazo dye of Comparative Example 1 Comparative Example 4; concentrated liquid of disazo dye of Comparative Example 2 Example 11; concentrated liquid of mixed dyes f to j Mixed dye f; disazo dye of Comparative Example 1 : disazo dye of Comparative Example 2 = 5 : 5 Mixed dye g; disazo dye of Comparative Example 1 : disazo dye of Comparative Example 2 = 6 : 4 Mixed dye h; disazo dye of Comparative Example 1 : disazo dye of Comparative Example 2 = 4 : 6 Mixed dye i; disazo dye of Comparative Example 1 : disazo dye of Comparative Example 2 = 7 : 3 mixed dye j; disazo dye of Comparative Example 1 : disazo dye of Comparative Example 2 = 3 : 7						

Next, the ink composition is explained concretely.

The ink compositions of Examples 12 to 20 and Comparative Examples 5 to 7 were prepared in mixing ratios shown in Table 3 according to the above-mentioned ink production method. Here, each ink component shown in the table is indicated in % by weight in total ink weight, and the residue is water.

[Table 3]

Ink composition		Example 12	Example 13	Example 14	Example 15	Example 16	Example 17
Dye concentrated liquid	A	16 (2.3)		40 (6.0)			
	B						
	E				50 (7.5)		42 (5.0)
	a						
Mixed dye concentrated liquid	b						
	F					50 (7.5)	
	G						
	J		16 (2.3)				
Diethylene glycol							
Polyethylene glycol A200			5		10	5	
1,5-pentane diol						5	
Glycerin		5		10			10
2-pyrrolidone		5		5		10	5
1,3-dimethyl-2-imidazolidinone			3		6		
Diethylene glycol monobutyl ether							
Triethylene glycol monobutyl ether							
Propylene glycol monobutyl ether							
Triethanolamine							
Potassium hydroxide			0.1	0.5			0.5
Ethanol		4					
1-propanol			3				
Surfinol 465					1		
Olfen STC				1		0.8	1
Sodium alginate			0.01				
Antifungal agent		0.3	0.3	0.3	0.3	0.3	0.3

Number in () indicates solid component.

[Table 4]

Ink composition		Example 18	Example 19	Example 20	Comparative Example 5	Comparative Example 6	Comparative Example 7
Dye concentrated liquid	A	40 (6.0)	50 (7.5)		1		16 (2.3)
	B						
	E						
	a				40 (6.0)		
	b					40 (6.0)	
Mixed dye concentrated liquid	F						
	G			50 (7.5)			
	J						
Diethylene glycol			10	5			
Polyethylene glycol A200				5			
1,5-pentane diol				5			
Glycerin		10			10	10	5
2-pyrrolidone		5		10	5	5	
1,3-dimethyl-2-imidazolidinone			8				
Diethylene glycol monobutyl ether		10			10	10	
Triethylene glycol monobutyl ether			10				
Propylene glycol monobutyl ether							
Triethanolamine		0.5			0.5	0.5	
Potassium hydroxide							
Ethanol							4
1-propanol							
Surfinol 465			1				
Olfin STG		1		0.8	1	1	
Sodium alginate							
Antifungal agent		0.3	0.3	0.3	0.3	0.3	0.3

Number in () indicates solid component.

In evaluation tests, inkjet printer MJ-700V2/C (made by Seiko-Epson Corp.) was used. That is, a black ink cartridge for MJ-700V2/C was charged with each ink of Examples 12 to 20 and Comparative Examples 5 to 7, evaluations were made on the following Tests 1 to 5.

(Test 1: water resistance)

Alphabet letters were printed on (1) EPP paper (acid paper; available from Epson Sales Corp.) and (2) Xerox P (neutral paper; available from Fuji Xerox Corp.), and water was dropped on the printed letters and air-dried. The condition of the letters was visually observed, and evaluated as follows.

- ⊙: no change as compared to the initial condition.
- : slight bleeding of dye, but letter is clearly legible.
- △: despite bleeding, letter is legible.
- ✕: letter is illegible due to bleeding.

(Test 2: image quality)

(2-1)

Alphabet letters and graphical pattern were printed on the following test papers, and they were evaluated as follows, by measurement of optical density (OD value) of solid part and visual observation.

- (1) EPP paper (Epson Sales Corp.)
- (2) Xerox P (Fuji Xerox Corp.)
- (3) Xerox 4024 (Xerox Corp.)
- (4) Ricopy 6200 (Ricoh Corp.)

Meanwhile, for measuring OD value, reflection density was measured by using Macbeth TR-927 (made by Macbeth Corp.).

- ⊙: no bleeding and OD value is not less than 1.30.
- : slight bleeding is observed, but there is no influence on the image, and OD value is not less than 1.25.
- △: a little bleeding, but OD value is less than 1.25.
- ✕: OD value is less than 1.20.

(2-2)

Colour printing was conducted on the following papers, and bleeding into the neighboring colour ink was visually evaluated.

- (1) EPP paper (Epson Sales Corp.)
- (2) Xerox P (Fuji Xerox Corp.)
- (3) Xerox 4024 (Xerox Corp.)
- (4) Ricopy 6200 (Ricoh Corp.)

- ⊙: no bleeding and clear
- : slight bleeding, but clear
- △: relatively noticeable bleeding
- ✕: intense bleeding

(Test 3: clogging recovering ability)

After charging of an ink into a recording head of MJ-700V2/C, the recording head was allowed to stand for one month at 40°C, being shifted from the cap position. After that, cleaning times required to enable normal printing was counted and evaluated as follows.

- ⊙: 0 to 2 times
- : 3 to 5 times
- △: 5 to 10 times
- ✕: can not recover by 10 times

(Test 4: printing stability)

Continuous printing was conducted using self check pattern loaded on MJ-700V2/C, and stable printing time was evaluated as follows.

- ⊙: not less than 24 hours
- o: not less than 10 hours and less than 24 hours
- x: less than 10 hours

(Test 5: storage stability)

The ink cartridge for MJ-700V2/C was charged with an ink, and allowed to stand for two weeks at -30°C and 70°C, and before and after that time, physical property, colour tone change, extraneous material and deposit appearance of ink were observed and evaluated as follows.

- o: no change in physical property and colour tone, and no appearance of extraneous material and deposit.
- x: change in physical property or colour tone, or appearance of extraneous material or deposit.

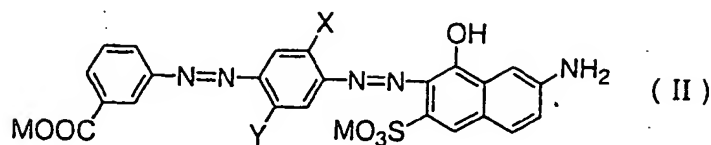
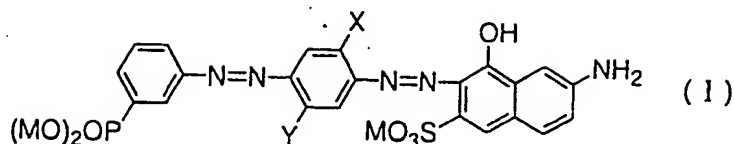
Evaluation results of the above-mentioned tests 1 to 5 are shown in Table 5.

[Table 5]

Test item	Ink	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Comparative Example 5	Comparative Example 6	Comparative Example 7
		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Test 1 Water resistance	(1)	○	○	○	○	○	○	○	○	○	○	○	○
	(2)	○	○	○	○	○	○	○	○	○	○	○	○
Test 2-1 Image quality	(1)	○	○	○	○	○	○	○	○	○	○	○	○
	(2)	○	○	○	○	○	○	○	○	○	○	○	○
	(3)	○	○	○	○	○	○	○	○	○	○	○	○
	(4)	○	○	○	○	○	○	○	○	○	○	○	○
Test 2-2 Bleeding	(1)	△	△	△	△	△	△	△	△	△	△	△	△
	(2)	△	△	△	△	△	△	△	△	△	△	△	△
	(3)	△	△	△	△	△	△	△	△	△	△	△	△
	(4)	△	△	△	△	△	△	△	△	△	△	△	△
Test 3 Clogging recovering ability	(1)	○	○	○	○	○	○	○	○	○	○	○	○
	(2)	○	○	○	○	○	○	○	○	○	○	○	○
	(3)	○	○	○	○	○	○	○	○	○	○	○	○
	(4)	○	○	○	○	○	○	○	○	○	○	○	○
Test 4 Printing stability	(1)	○	○	○	○	○	○	○	○	○	○	○	○
	(2)	○	○	○	○	○	○	○	○	○	○	○	○
Test 5 Storage stability	(1)	○	○	○	○	○	○	○	○	○	○	○	○
	(2)	○	○	○	○	○	○	○	○	○	○	○	○

Claims

1. A disazo dye composition comprising at least a disazo dye represented by formula (I) and a disazo dye represented by formula (II):



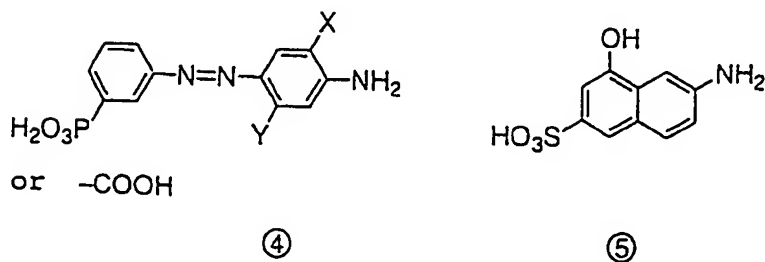
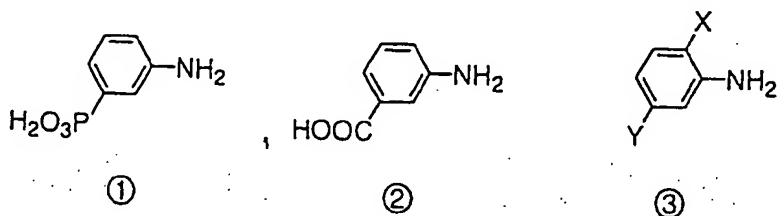
(wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of alkaline metal, NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium and piperidinium),

wherein, when the disazo dye composition is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by formula (I) to the peak area (Sc) of the disazo dye represented by formula (II), that is $\text{Sp} : \text{Sc}$ is from 1 : 0.4 to 1 : 2.4.

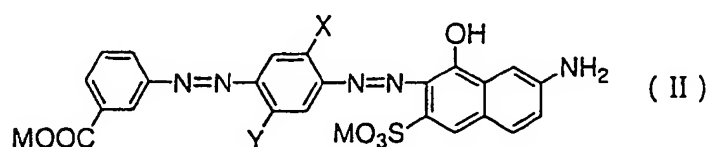
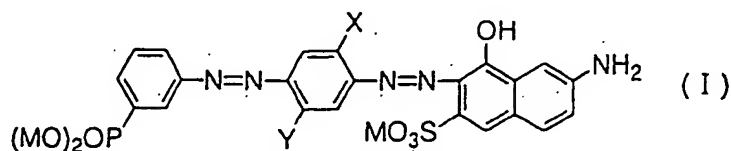
2. The disazo dye composition according to claim 1, wherein the area ratio $\text{Sp} : \text{Sc}$ is from 1 : 0.6 to 1 : 1.5.

3. A method for producing the disazo dye composition of claim 1 or 2, comprising the steps of:

simultaneously diazotizing a mixed amine comprising m-aminobenzenephosphonic acid ① and m-aminobenzenecarboxylic acid ② in a molar ratio ① : ② of from 1 : 0.4 to 1 : 2.5 and coupling with 2,5-dialkoxy-substituted aniline ③ to obtain a monoazo compound ④, and diazotizing thus obtained monoazo compound ④ and coupling with γ acid ⑤:



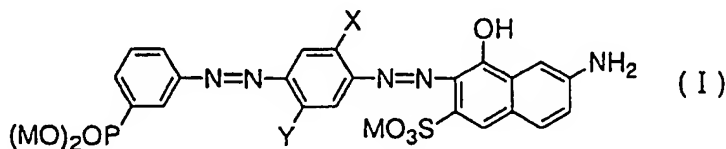
4. Dye concentrated liquid which comprises not less than 10% by weight of the disazo dye composition of claim 1 or 2.
5. A black aqueous ink composition comprising at least a disazo dye represented by formula (I) and a disazo dye represented by formula (II):

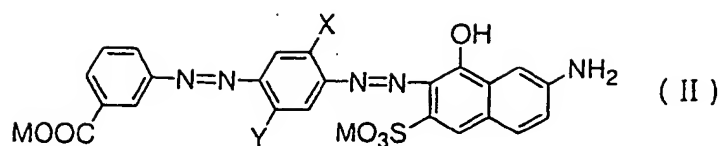


(wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of alkaline metal, NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium and piperidinium),

wherein, when the black aqueous ink is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by formula (I) to the peak area (Sc) of the disazo dye represented by formula (II), that is $\text{Sp} : \text{Sc}$ is from 1 : 0.4 to 1 : 2.4.

6. The black aqueous ink composition according to claim 5, wherein the area ratio $\text{Sp} : \text{Sc}$ is from 1 : 0.6 to 1 : 1.5.
7. The black aqueous ink composition according to claim 5 or 6, which further comprises a polyhydric alcohol and a nitrogen-containing cyclic compound.
8. The black aqueous ink composition according to any of claims 5 to 7, which further comprises a nonionic acetylene glycol surface active agent.
9. The black aqueous ink composition according to any of claims 5 to 8, which further comprises glycol ethers.
10. An inkjet recording method in which the ink is discharged through fine orifices as droplets to record on a recording medium, wherein the ink comprises at least a disazo dye represented by formula (I) and a disazo dye represented by formula (II):





10 (wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of alkaline metal, NH_4 , alkyl-substituted ammonium, alkanolammonium, morpholinium and piperidinium), and, when the ink is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by formula (I) to the peak area (Sc) of the disazo dye represented by formula (II), that is $\text{Sp} : \text{Sc}$ is from 1 : 0.4 to 1 : 2.4.

15 11. The inkjet recording method according to claim 10, wherein the area ratio $\text{Sp} : \text{Sc}$ is from 1 : 0.6 to 1 : 1.5.

20 12. The inkjet recording method according to claim 10 or 11, wherein the ink comprises a polyhydric alcohol, a nitrogen-containing cyclic compound, a nonionic acetylene glycol surface active agent, and a glycol ether, in addition to the disazo dyes represented by formulae (I) and (II).

Fig. 1

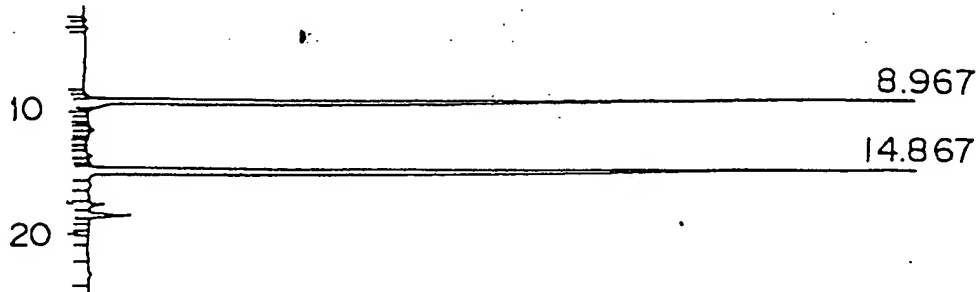


Fig. 3

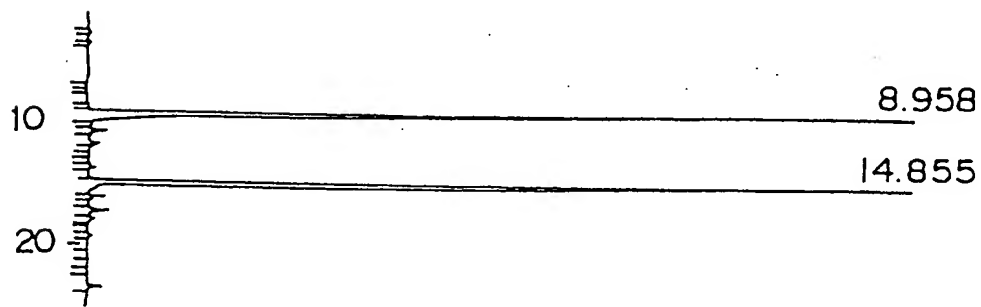


Fig. 4

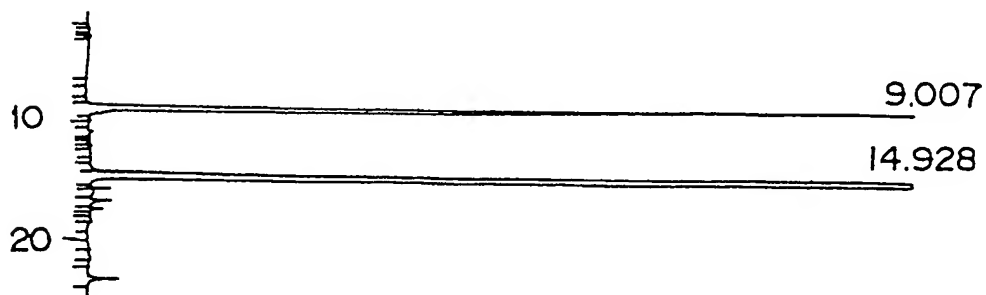


Fig. 2

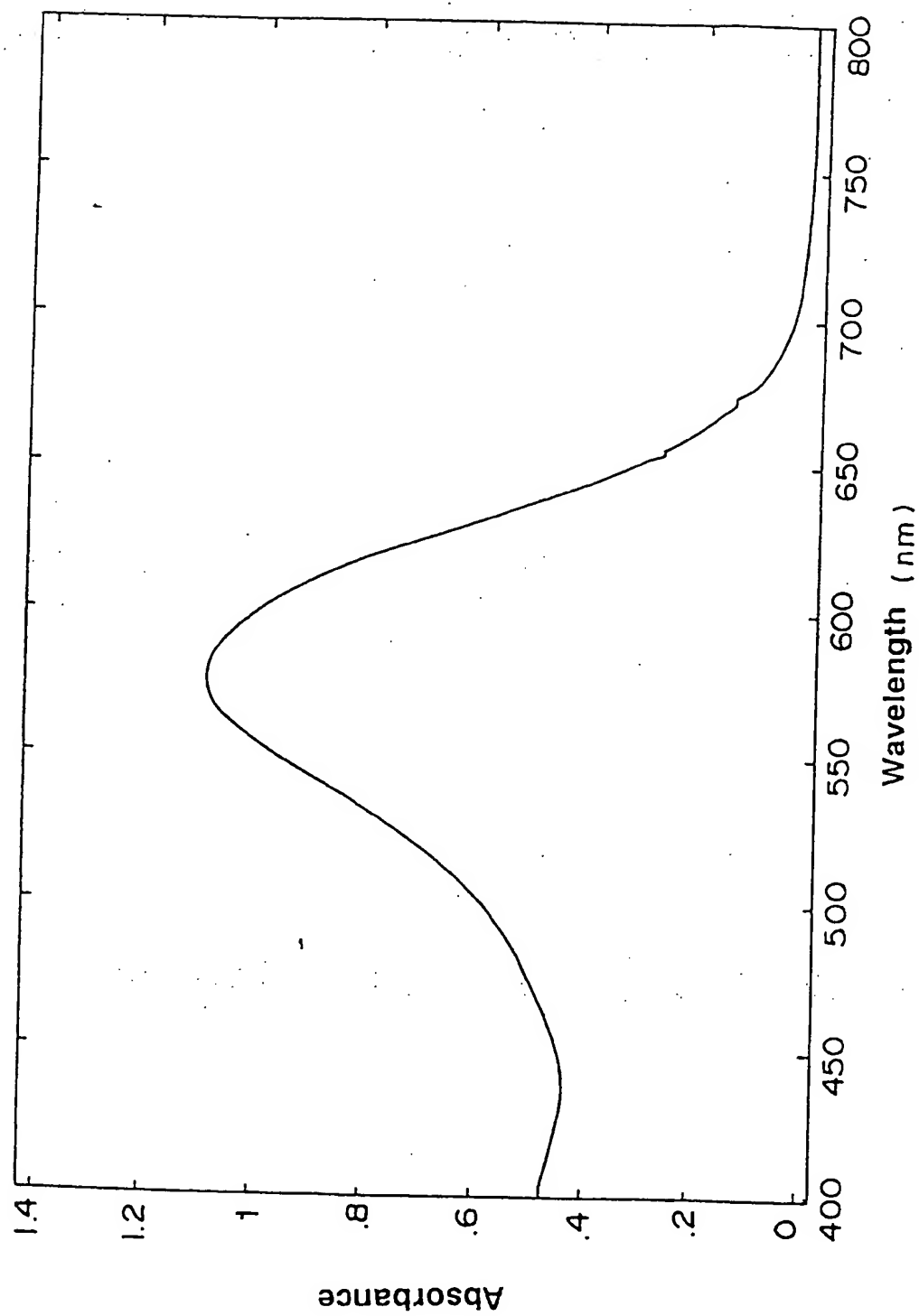


Fig. 5

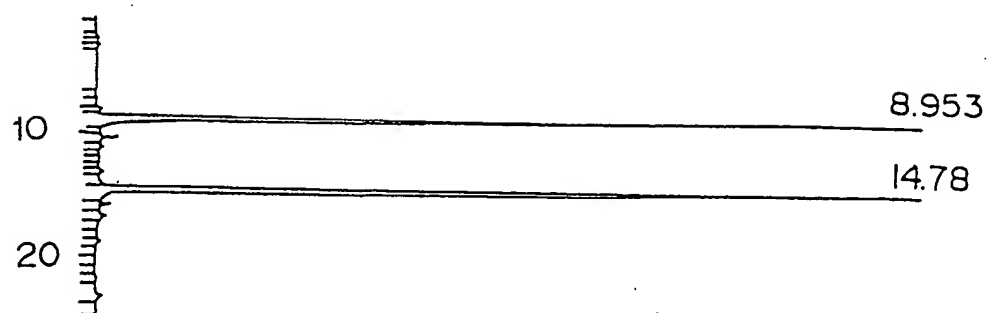


Fig. 6

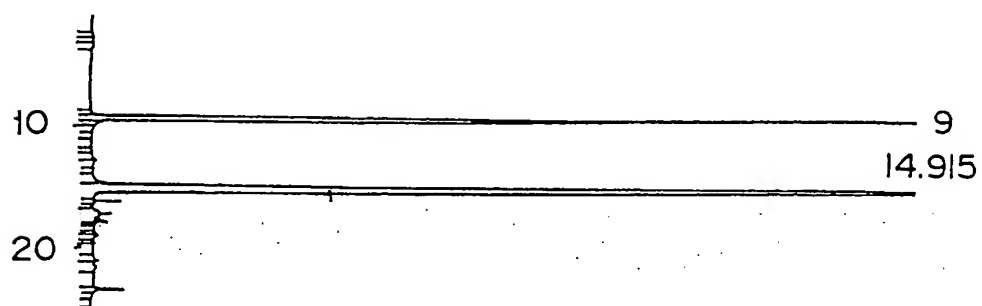


Fig. 7

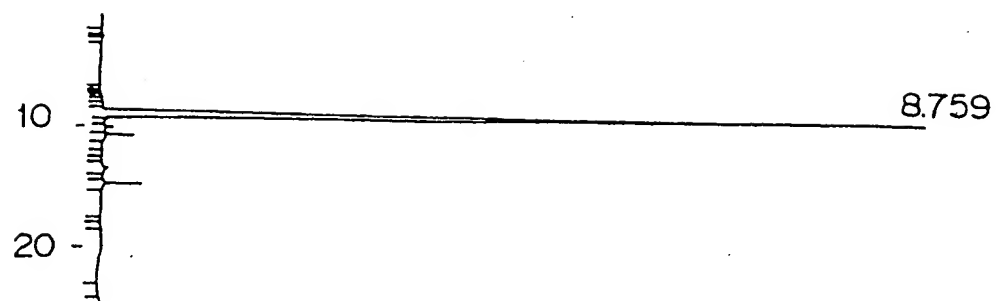


Fig. 9

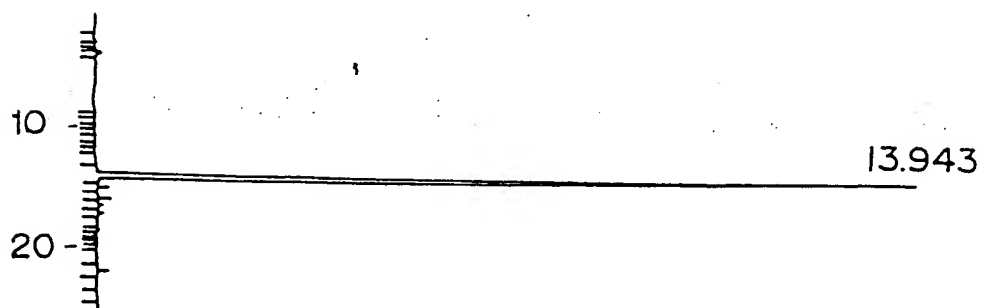


Fig. 8

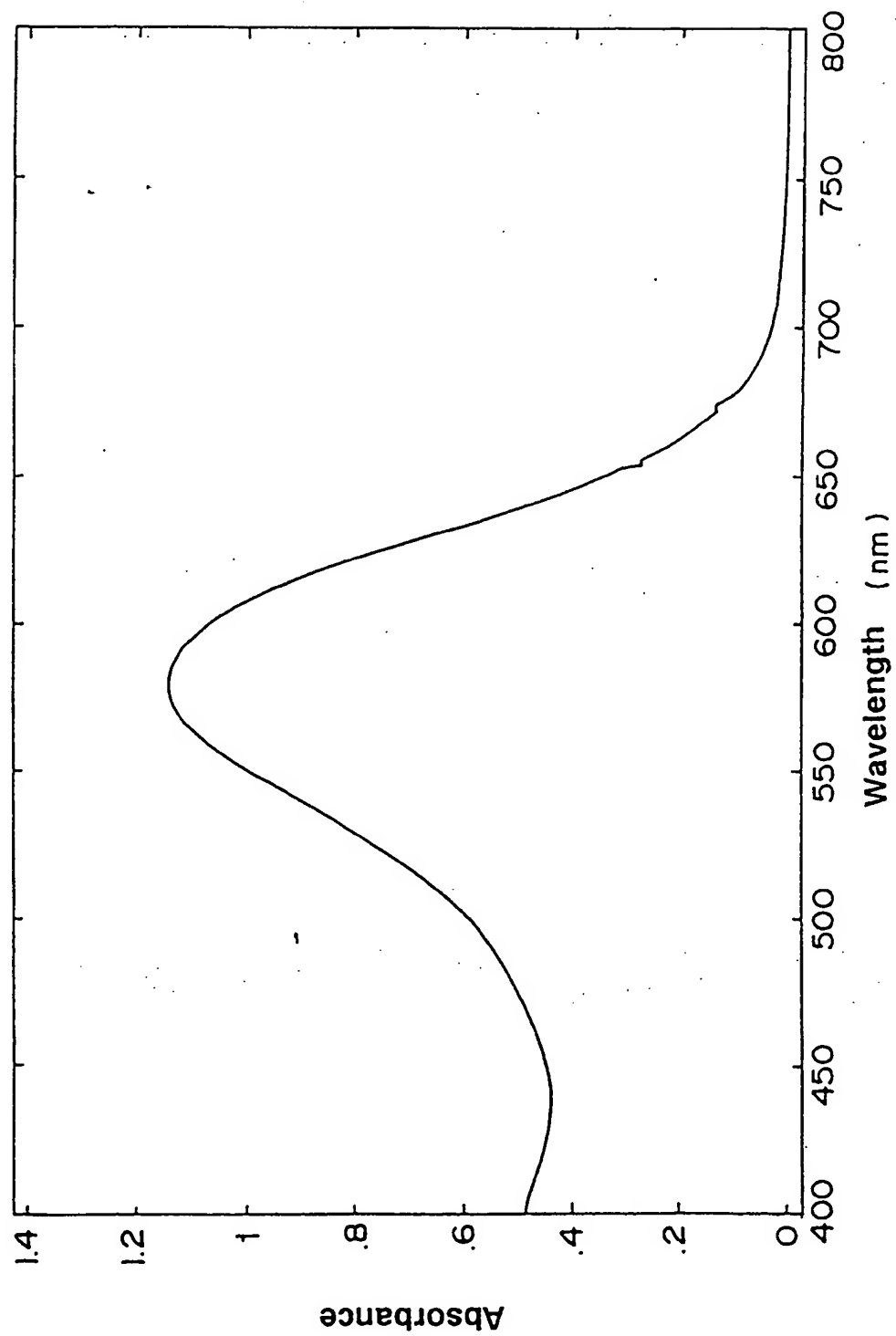


Fig. 10

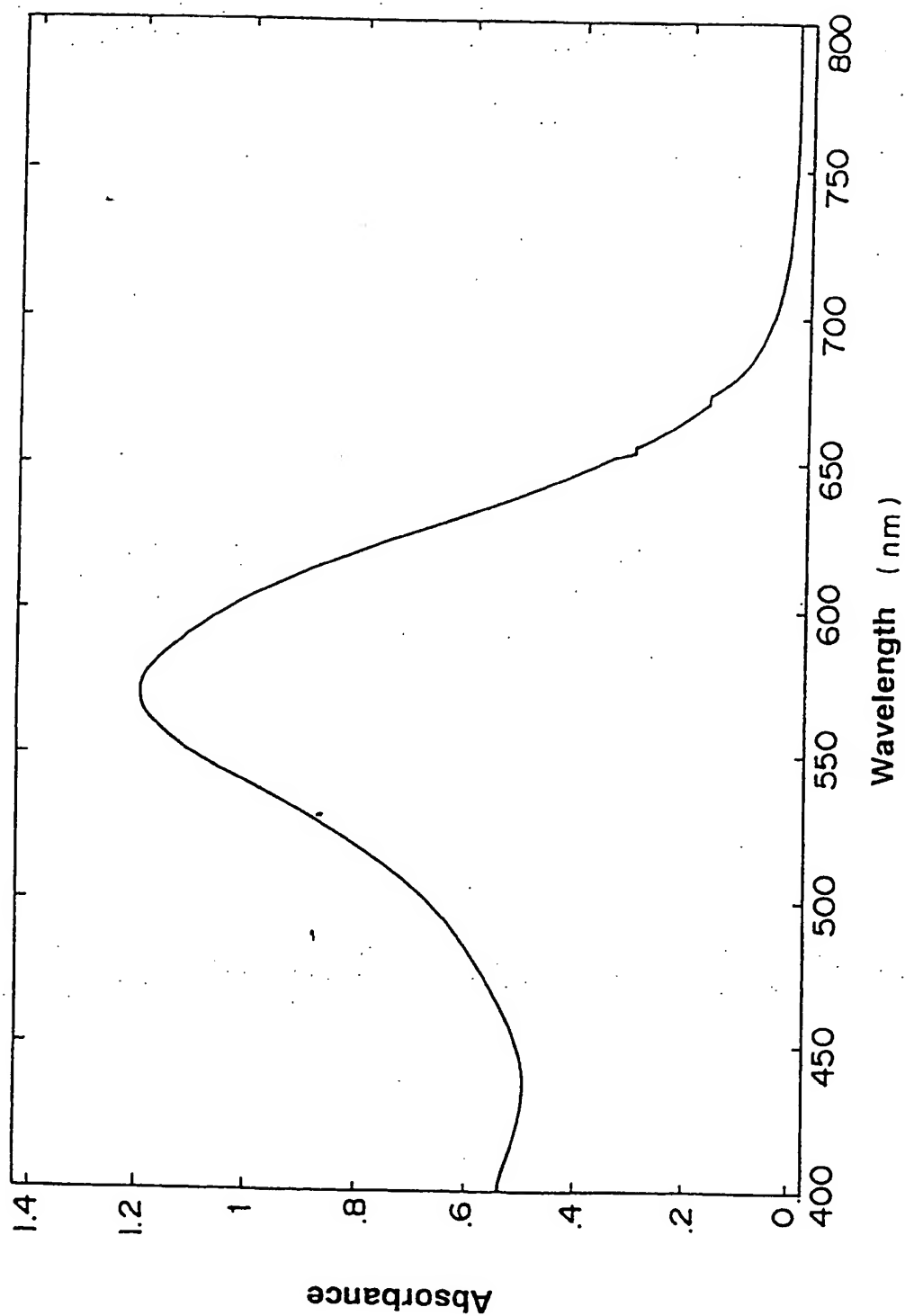


Fig. 11

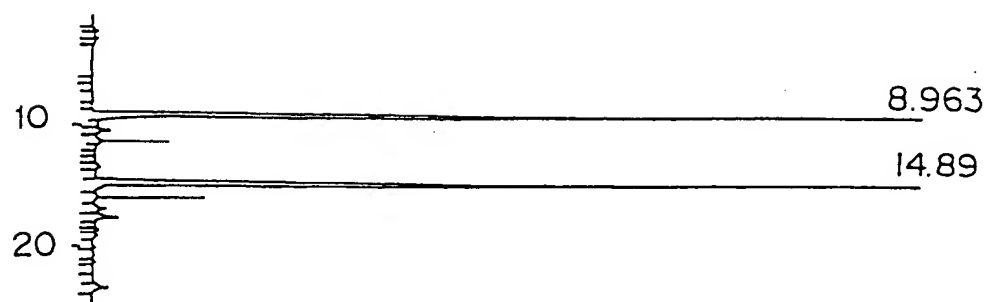
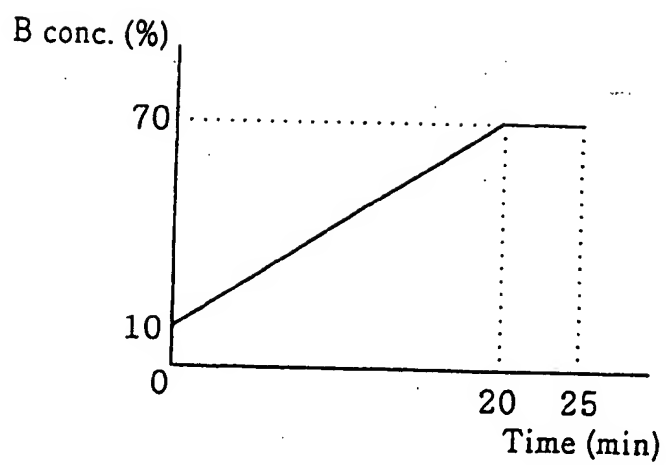
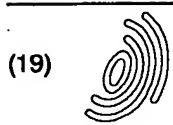


Fig. 12





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(12) EUROPEAN PATENT APPLICATION

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(71) Applicant: ORIENT CHEMICAL INDUSTRIES, LTD.
Osaka-shi Osaka-fu (JP)

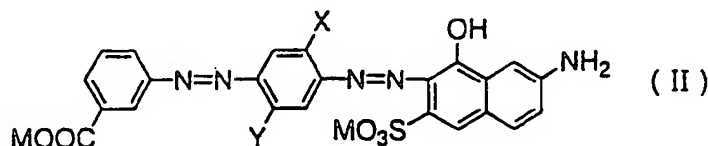
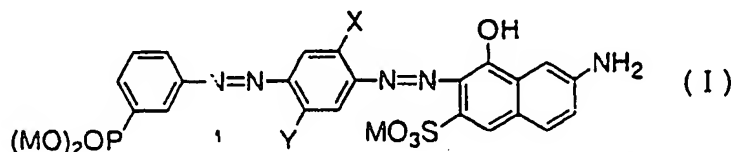
(72) Inventors:
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(54) Disazo-dye composition and black aqueous ink composition containing the same

(57) A disazo dye composition comprising at least a disazo dye represented by formula (I) and a disazo dye represented by formula (II);



(wherein X and Y indicate an alkoxy group having 1 to 4 carbon atoms, and M indicates hydrogen or a cation selected from the group consisting of, alkaline metal, NH₄, alkyl-substituted ammonium, alkanolammonium, morpholinium and piperidinium), wherein, when the disazo dye composition is analyzed by liquid chromatography, the area ratio of the peak area (Sp) of the disazo dye represented by formula (I) to the peak area (Sc) of the disazo dye represented by for-

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mula (II), that is $S_p : S_c$ is from 1 : 0.4 to 1 : 2.4. This disazo dye composition provides a high quality image, rapid ink fixing and the like even on the plain paper.



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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 3585

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 463 737 A (HEWLETT PACKARD COMP.) * page 4, line 42 - line 45; tables *	1-12	C09B67/22 C09B67/26 C09B31/08 C09D11/00
A	EP-0 491 993 A (ORIENT CHEMICAL IND.) * page 12, table 1, examples 7,8 *	1-12	
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D	& JP 05 125 318 A		
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A	EP 0 539 178 A (ORIENT CHEMICAL IND.) * abstract * * page 2, line 30 - page 3, line 11; examples 4,5 *	1,5,10	
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09B C09D
Place of search		Date of completion of the search	Examiner
THE HAGUE		19 March 1997	Ketterer, M
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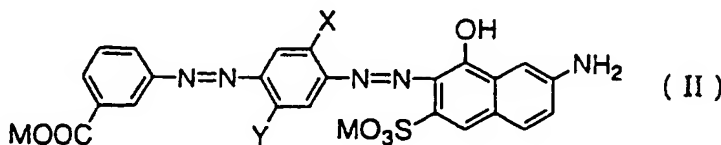
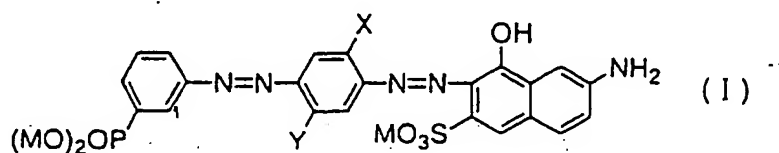
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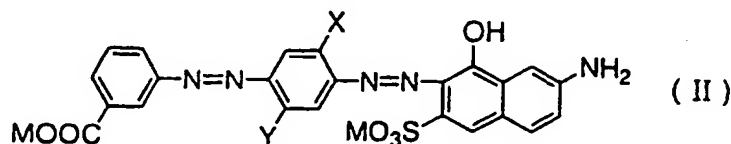
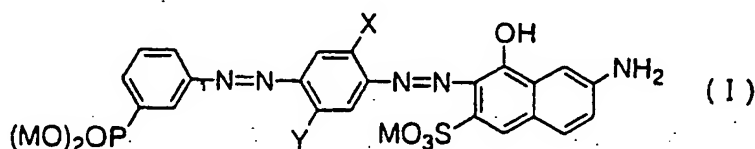
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